GEOMAR
Helmholtz-Zentrum für
Ozeanforschung Kiel

Date: 14.12.2018

Cruise Report

Compiled by: Dr. Dennis Booge

F.S. Alkor **Cruise No.: AL 510**

Dates of Cruise: 03.06.2018 – 15.06.2018

Areas of Research: Physical, chemical, biological oceanography / Atmospheric chemistry

Port Calls: none

Institute: GEOMAR Helmholtz Centre for Ocean Research Kiel

Chief Scientist: Dr. Dennis Booge

Number of Scientists: 12

Projects: US NSF (title: Collaborative Research: Influence of Surfactants on Air-Sea Gas Exchange: $^3He/SF_6$ Experiments in the Baltic Sea)

DOI 10.3289/CR_AL510.

Cruise Report

This cruise report consists of 23 pages including cover:

1. Scientific crew

Name	Function	Institute	Leg
Dr. Dennis Booge	Chief Scientist	GEOMAR	Entire cruise
Prof. Dr. David Ho	Scientist	University of Hawaii	Entire cruise
Dr. Toby Koffman	Scientist	Columbia University	Entire cruise
Dr. Tim Fischer	Scientist	GEOMAR	Entire cruise
James Ash	Technician	University of Hawaii	Entire cruise
Benjamin Hickman	Technician	University of Hawaii	Entire cruise
Tim Georg Steffens	Technician	GEOMAR	Entire cruise
Jon Roa	Technician	GEOMAR	Entire cruise
Li Zhou	PhD Student	GEOMAR	Entire cruise
Florian-David Lange	PhD Student	University of Kiel	03.06. - 07.06.2018
Melf Paulsen	Master Student	GEOMAR	Entire cruise
Theresa Barthelmeß	Master Student	GEOMAR	Entire cruise
Nhat-Thao Ton-Nu	Bachelor Student	University of Kiel	07.06. - 15.06.2018
Total	**13**		

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2. Research programme

Air-sea gas exchange influences the cycling of biogeochemically important trace gases on global and regional scales (CO_2, DMS, halocarbons, and non-methane hydrocarbons), and affects water quality on local scales (e.g., oxygen exchange). Wind speed is typically used to parameterize gas transfer and, in the last few decades, advancements in field and analysis techniques have enabled us to narrow the list of reasonable wind speed/gas exchange parameterizations that are applicable in most circumstance over the ocean. However, there are environments and conditions where existing parameterizations might not be applicable. One of these environments is inland seas where surfactants might have a more dominant effect on gas exchange.

All the studies published to date that have investigated the effects of surfactants on air-sea exchange have either used artificial surface active compounds or have only measured surfactant and wave properties under natural conditions, rather than gas transfer or flux directly. This cruise, the first of two "Baltic GasEx" cruises, aimed to close that gap by conducting direct air-sea transfer measurements in the presence of natural surfactants at the Baltic Sea time series station, Boknis Eck, where natural surfactant measurements have been recorded from 2009-2014 using surface-sensitive sum-frequency generation spectroscopy. We used two different methods, simultaneously, to directly measure the gas exchange:

1) *$^3He/SF_6$ tracer release experiment:*

   Using this technique a mixture of $^3He/SF_6$ gas is directly bubbled into the mixed layer via diffusion tubing. SF_6 and ^3He concentrations in the tracer patch will be monitored for 7-10 days following injection. As both gases have different solubilities in seawater the concentration change, as well as the ratio change over time will be used to calculate the gas transfer coefficient.

2) *Trace gas eddy covariance:*

   The eddy covariance technique consists of computing the covariance between simultaneously measured vertical wind speed and gas concentration fluctuations at the frequencies of turbulent motion in the atmosphere (>2 Hz). This micrometeorological technique is a direct flux measurement technique. Typically, the gas measurements are made at 10 Hz and the wind measurements at 30-50 Hz. The covariance is averaged between 10 and 60 minutes. Because measurements are performed on a moving platform, the measured vertical wind speed needs to be corrected for the motion of the ship. The influence of flow distortion is omitted by using only the periods with optimal apparent wind directions (±60 degrees from the bow of the ship, (e.g., MARANDINO et al., 2007)).

In conjunction with gas exchange measurements, the abundance of surface active compounds was quantified and characterized in order to determine the influence of surfactants/microlayer on the air-sea fluxes. Furthermore, gas transfer parameterizations based on wind speed will be evaluated, both for the influence of surfactants and the difference between the open ocean and inland seas.

After injection of the tracer gas mixture, the moving patch was constantly monitored using a fully automated high-resolution SF_6 analysis system. Big CTD stations (Figure 1) were carried out twice a day in the tracer patch in order to investigate the vertical distribution of physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters. At the same time, samples for surfactants and organic matter in the surface microlayer were taken from the rubber boat. Additionally, in between the big CTD stations, two small CTD stations were carried out in order to assess changes in the mixed layer depth. Atmospheric concentrations of CO_2 and DMS were recorded continuously at ~9 m from the sea surface from an air inlet attached to a mast at the bow of the ship.

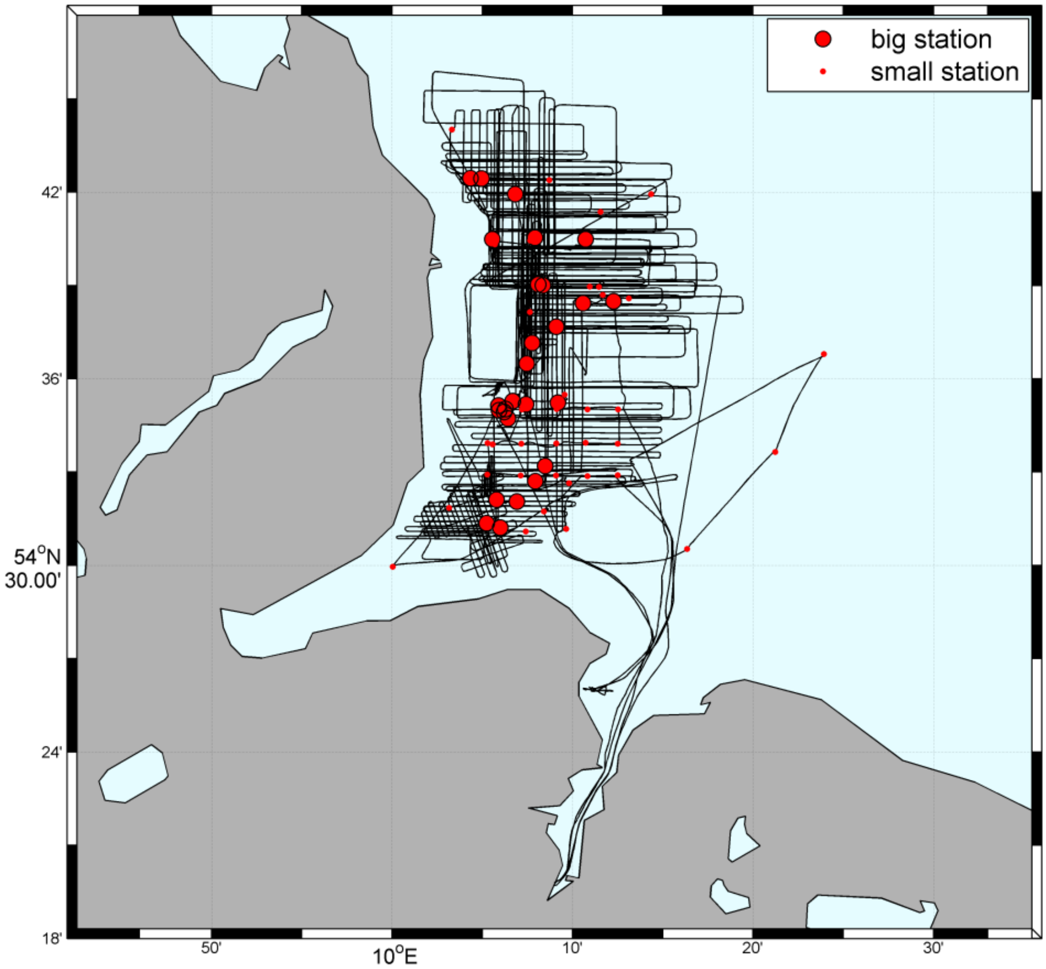

Figure 1: Cruise track of AL510 including CTD stations. Big station: CTD station including full physical, chemical and biological characterization of the water column including rubber boat samplings. Small station: CTD station without water sampling.

3. Narrative of cruise with technical details

Sunday, 03.06.2018

The first day of the cruise was used to find the best location for injection of the tracer gas mixture. The research area was systematically mapped by performing half hourly small CTD stations in order to get information about the MLD. The ADCP of the Alkor was used to determine current directions and velocities. Furthermore, a drifter was deployed during the day in order to follow the same water mass and give additional information about current directions and velocities.
During the day, continuous underway measurements monitoring the sea surface for temperature, salinity, chl-a, CDOM, SF_6 and pCO_2 were started. Furthermore, 1-3 hourly discrete sampling from the underway line for trace gases, nutrients and CDOM began.

08:00	Departure Kiel
10:06	Drifter in water in order to check currents
10:53 - 12:49	4 small stations - check MLD and currents
13:34	Drifter back on deck
14:46	Big station This “test” station was used to check sampling procedures and get information about the vertical distribution of chemical, physical and biological parameters.
15:34	Drifter in water in order to check currents
16:00	rubber boat sampling
17:04	Small station - check MLD and currents
18:13	Drifter back on deck
20:04 - 23:52	10 small stations - check MLD and currents

Monday, 04.06.2018

Continuous eddy covariance measurements for CO_2 were started.

00:10 - 12:16	6 Small stations - check MLD and currents
13:28	Big station including rubber boat sampling at the determine site for tracer injection Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension), before the injection of the tracer gas mixture in order to characterize the natural background.
17:38 - 18:08	Injection of the tracer gas mixture at 54°35 N and 10°06 E

Tuesday, 05.06.2018

From this day on the daily working routine was mostly the same for the rest of the cruise consisting of two big stations at about 6am/6pm (duration ~ 3 hours) and two small stations at noon and midnight (duration ~ 20 min). In between those stations, the location and expansion of the tracer patch was constantly mapped using the underway SF_6 system.

06:08 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:04 Small station - check MLD and currents

17:57 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

23:55 Small station - check MLD and currents

Wednesday, 06.06.2018

06:07 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:05 Small station - check MLD and currents

18:06 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Thursday, 07.06.2018

Continuous eddy covariance measurements for DMS were started.

00:02 Small station - check MLD and currents

05:53 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

09:53 Drifter in water

10:00 - 12:00 Meeting with FB Polarfuchs:
Sampling of the water column for trace gases and CDOM on port side, starboard side and in the EC footprint (~0.5 miles in front) of the Alkor in order to investigate the heterogeneity of the water mass with respect to the sampled trace gases

12:10 Small station - check MLD and currents

15:01 Drifter on deck

18:09 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Friday, 08.06.2018

00:02 Small station - check MLD and currents

06:01 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

07:37 Drifter in water

10:00 - 12:00 Meeting with FB Polarfuchs:
Sampling of the water column for trace gases and CDOM on port side, starboard side and in the EC footprint (~0.5 miles in front) of the Alkor in order to investigate the heterogeneity of the water mass with respect to the sampled trace gases

12:02 Small station - check MLD and currents

17:19 Drifter on deck

18:03 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Saturday, 09.06.2018

00:05 Small station - check MLD and currents

06:02 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a,

nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:04	Small station - check MLD and currents
18:03	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Sunday, 10.06.2018

00:04	Small station - check MLD and currents
06:01	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)
07:21	Drifter in water
12:01	Small station - check MLD and currents
17:41	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)
19:52	Drifter on deck
23:58	Small station - check MLD and currents

Monday, 11.06.2018

05:59	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)
12:07	Small station - check MLD and currents
17:58	Big station Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^3He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters
20:10	Small station - check MLD and currents

Tuesday, 12.06.2018

00:04	Small station - check MLD and currents
06:01	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)
07:26	Drifter in water
12:01	Small station - check MLD and currents
17:57	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)
20:20	Drifter accident at 54°39N, 10°11E: When trying to get the drifter back on deck, the lower portion was caught in the propeller of the ship. The crew was not able to free the drifter from the propeller and ship was unable to navigate. The anchor was dropped for the night.

Wednesday, 13.06.2018

00:02	Small station - check MLD and currents
06:06	Big station Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters
09:30	Heading back to Kiel using the pump jet of the Alkor
13:48 - 15:36	Scientific divers free propeller from destroyed drifter Left Kiel to return to research area
18:38	Big station Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters

Thursday, 14.06.2018

00:05	Small station - check MLD and currents
06:00	Big station including rubber boat sampling Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a,

nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

12:05 Small station - check MLD and currents

18:04 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

Friday, 15.06.2018

00:05 Small station - check MLD and currents

06:01 Big station including rubber boat sampling
Sampling of the water column for physical (e.g. temperature, salinity, pH), chemical (e.g. ^{3}He, SF_6, oxygen, trace gases) and biological (e.g. chl-a, nutrients) parameters, as well as the SML (e.g. surfactants, lipids, surface tension)

13:42 Arrival Kiel

4. Scientific report and first results

4.1 Hydrographic observations

CTD and salinity measurements and calibration

During AL510 62 profiles of pressure (p), temperature (T), conductivity (c) and oxygen (O) were recorded. These CTD-O_2 profiles usually ranged from the surface to 1 m above bottom, as recorded by the CTD-mounted altimeter (sn#453). We used a Seabird Electronics (SBE) 9plus system (IFM-GEOMAR Kiel SBE-2), attached to a 12-bottle water sampler rosette (SBE#1), and the latest Seabird Seasave software. SBE-2 had two sensor sets: p #80024, T1 #2463, c1 #2537, O1 #0215, T2 #5020, c2 #3366, O2 #2600. 80 salinity samples were taken in order to calibrate conductivity. The salinity samples are currently being analyzed with an Optimare salinometer. The samples seem to contain unusual amounts of some fatty compounds, which deposited on the glass of the salinometer conductivity cell. 112 oxygen samples were Winkler titrated. Final calibrated CTD data will be available after finalizing the salinity measurements. In addition, a Dr Haardt fluorescence sensor (sn#14010) was attached to the rosette, but was not calibrated.

Current observations

A vessel mounted Acoustic Doppler Current Profiler (ADCP) continuously recorded current velocities. The Nortek Signature 1000 kHz transducer was placed in the moon pool, aligned to 45 degrees. Ship heading data came via an extra GPS antenna mounted on the rear of the top deck. In combination with bottom tracking, the system produced current output already corrected for possible transducer misalignment. The configuration of the Signature 1000 was 60 bins of 0.5 m, pinging at 120 per minute. The system provided enough range for the maximum 25 m depth during the cruise. The first usable bin was at 5 m depth. The system worked well throughout the cruise and there were no issues with detection below the strong halocline or in oxygen depleted waters. The large issue was the ship itself interfering with the currents: during steaming the ship caused a considerable artificial current in direction to the rear of the ship, due to displacement and propulsion; during station work, the occasional maneuvering caused internal waves of considerable vertical amplitude. In essence, undisturbed records of the background current field could only be obtained when on station after settling of the maneuver-caused disturbances.

Microstructure measurements

A MSS90-L microstructure profiler (#028) of Sea and Sun Technology was used to infer turbulent dissipation rate and diapycnal diffusivity, aiming at quantifying diapycnal fluxes. The loosely tethered profiler was launched manually from the work boat during 19 ship stations, generally 3 microstructure profiles following the procedure of near-surface gas sampling. The profiler was equipped with 2 airfoil shear sensors and a fast thermistor, as well as with a pressure, conductivity, temperature, oxygen and turbidity sensor. Profiler sink velocity was adjusted to 0.65 m/s. In total 56 profiles were performed, delivering usable data usually from 2 m depth down to the bottom. Figure 2 shows a typical profile with increased near-surface and near-bottom mixing.

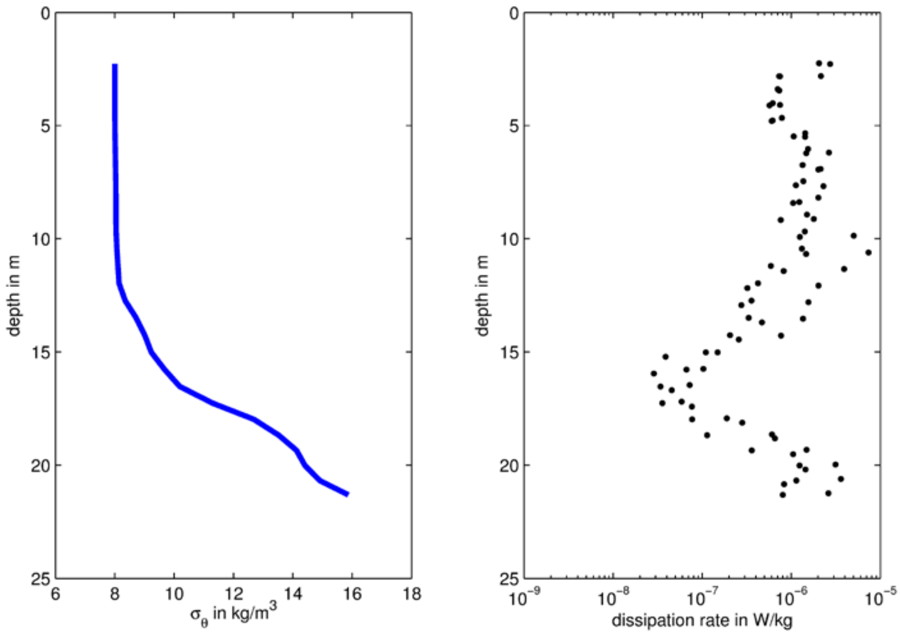

Figure 2: Depth profile of density (left) and dissipation rate (right) from microstructure sonde measurements from june 14th.

4.2 $^3He/SF_6$ tracer

After finding the best location (54°35 N and 10°06 E) for the tracer release during the first day, ^3He and SF_6 was injected into the water by bubbling a mixture of 5 L ^3He in 340 L of SF_6 into the water as the ship traversed two concentric hexagons with diameters of 300 and 585 m. Over the course of 20 minutes at a flow rate of 2 L min^{-1}, 40 L of the gas mixture was injection into the water.

Underway measurements of surface water SF_6 were made in order to locate the center of the tracer patch for the 6:00 and 18:00 CTD stations (Figure 3). The measurements were made on the water pumped from the ship's uncontaminated seawater intake using a continuous SF_6 system described in HO et al. (2002) and CAPLOW et al. (2004). The measurement interval was ca. 50 s.

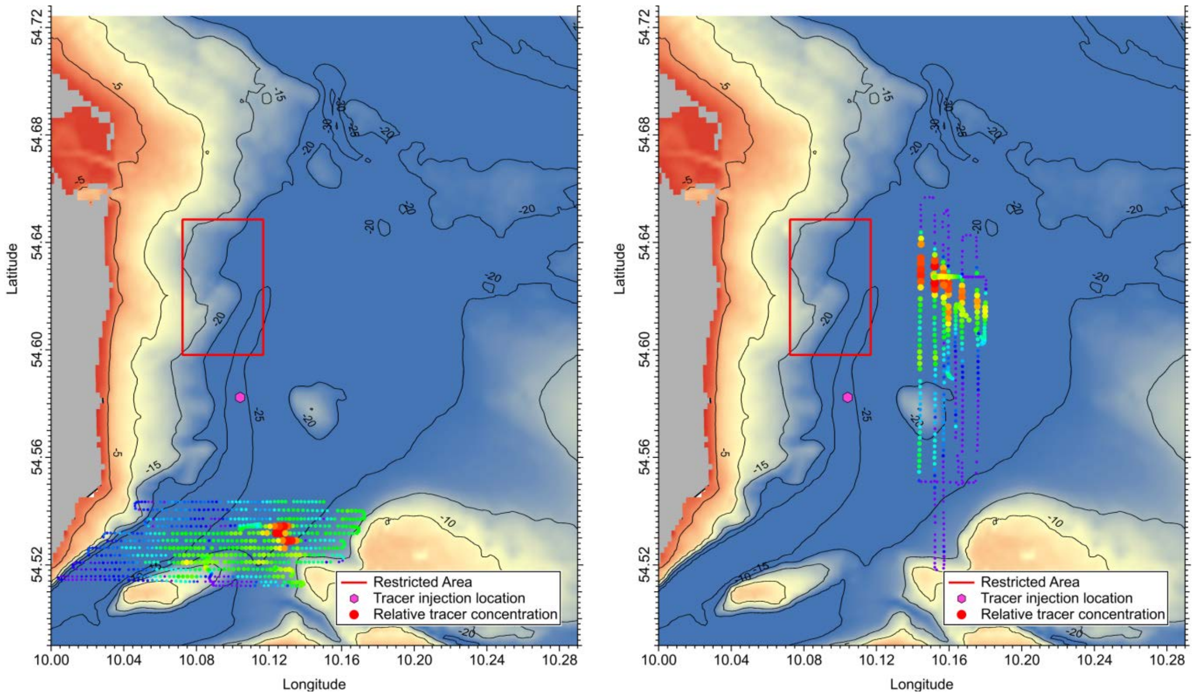

Figure 3: Two examples of underway SF_6 surveys (6am to 6pm) during AL510 on june 6th (left) and june 8th (right), respectively.

At each 6:00 and 18:00 CTD station, discrete ^3He and SF_6 samples were taken at 7 depths to determine gas transfer velocities during the cruise.. The ^3He samples were taken in cooper tubes (nominal volume of 40 mL) mounted in aluminum channels with stainless steel clamps, and SF_6 were taken in 550 mL borosilicate glass bottles with ground glass stoppers. The SF_6 samples were measured onboard the ship using a purge-and-trap gas chromatographic system, and the ^3He samples were shipped back to the laboratory for extraction and future analysis on a helium mass spectrometer.

Spreading oil

Besides underway chlorophyll a and CDOM measurements, a spreading oil technique was performed, to infer the presence of surfactants. Fifteen solutions of paraffin wax, each with varying concentrations of dodecanol, were used to make qualitative in situ surface tension measurements of seawater during each rubber boat station. The goal of the oil drop measurements was to determine in a qualitative sense the surface tension of seawater, which is a function of surfactant concentrations. Each solution was calibrated to spread at a particular surface tension. By placing a drop of each oil solution onto the water surface, watching to see which droplets spread or do not spread, the surface tension of the seawater can be bracketed between two discrete values roughly 1 mN m^{-1} apart. The measured surface tension varied from 71.9 to 73.9 mN m^{-1}, and was never significantly out of range of the predicted surface tension (Figure 4) indicating surfactants had little effect on the surface tension of the seawater for the duration of the cruise.

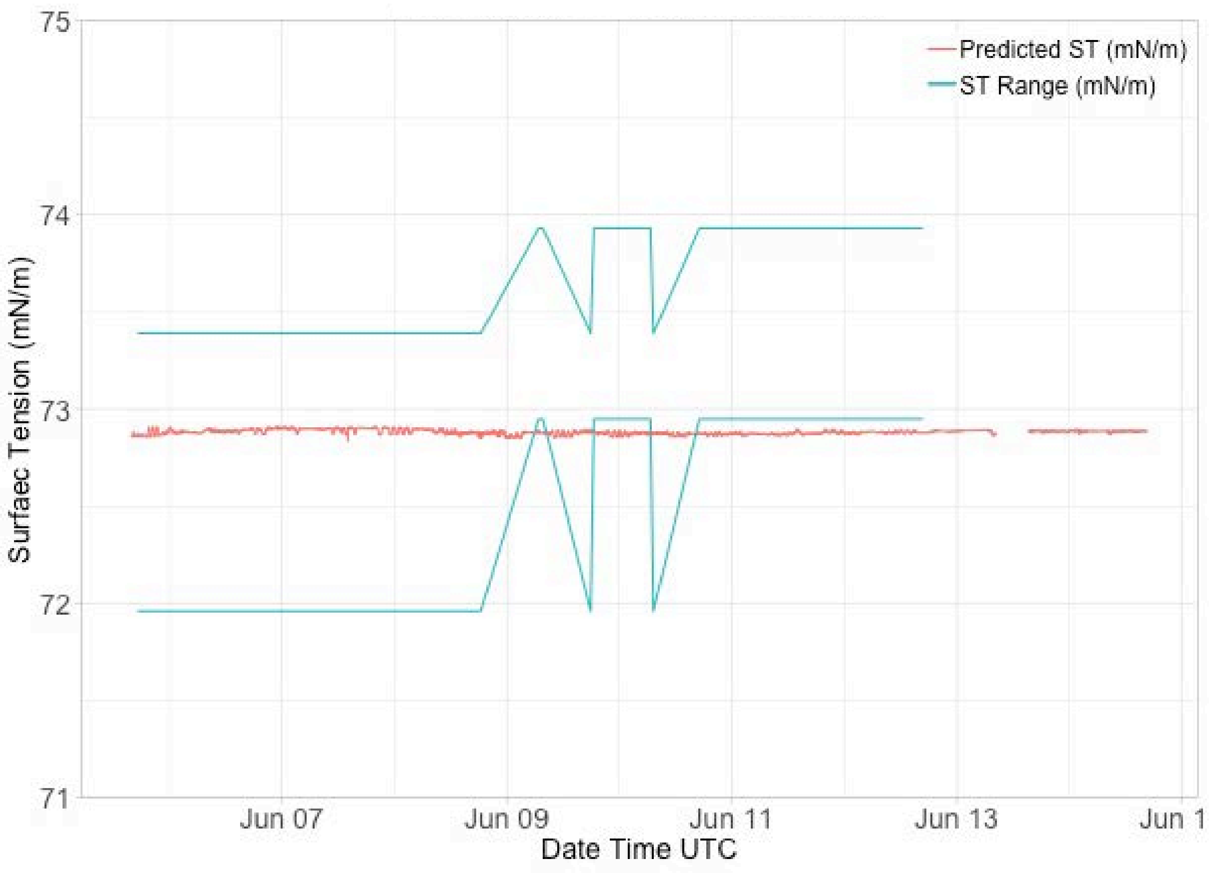

Figure 4: Predicted sea surface tension (red line) determined from measured sea surface salinity and temperature against the *in situ* surface tension measurements from the spreading oil method.

4.3 Air-sea gas exchange measurements

Direct gas flux measurements

During the cruise, CO_2 and DMS gas fluxes where conducted using the eddy covariance method. Therefore, a mast was set up on the bow of the ship equipped a CSAT-3 sonic anemometer to measure three dimensional wind speed, an inertial motion unit/GPS to determine the ship's motion, and inlets for gas sampling (Figure 5). Air was pumped from the mast through tubing to the measurement systems. Processing of the data is still being done.

Figure 5: Mast including sensors and air inlet at the bow of the Alkor.

Indirect gas flux measurements

In order to calculate air gas exchange of DMS indirectly, marine and atmospheric DMS concentrations were recorded. The DMS atmospheric data were recorded by a continuously running atmospheric pressure chemical ionization mass spectrometer (APCI-MS). Atmospheric DMS was sampled from the bow mast at 10 m height and 50 m of ½'' OD Teflon tubing at 60 L min^{-1} STP. Preliminary DMS hourly mean mixing ratios range from 127.70 to 666.99 ppt (Figure 6). The average is 307.85±127.70 ppt. The highest and the lowest values appeared on 11^{th} of june. The data has periodic daily changes; the concentration is usually higher at noon than at night.

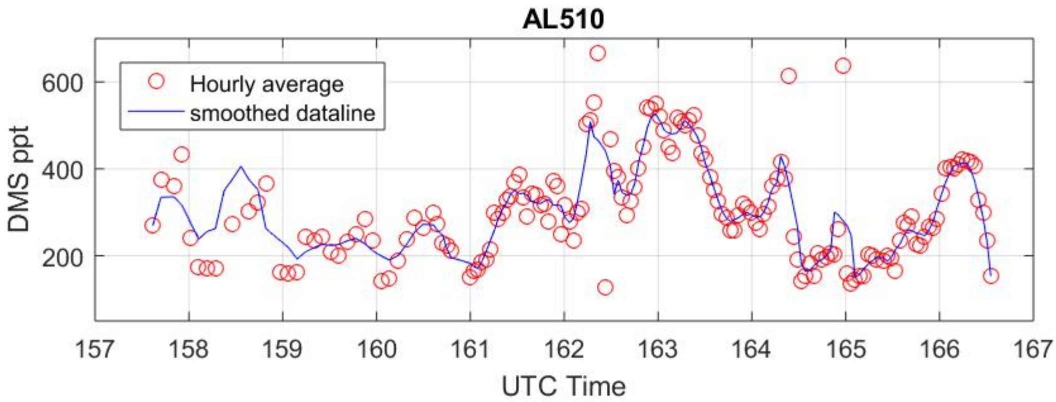

Figure 6: Time series of hourly mean atmospheric DMS mixing ratios during AL510.

Discrete samples for DMS and isoprene were taken hourly from the underway system (inlet: ~2 m depth) and measured using a purge and trap system connected to a gas chromatograph equipped with mass spectrometer for detection. The preliminary results in Figure 7 show an increase of surface DMS concentrations during the cruise from 2 nmol L^{-1} in the beginning up to 6 nmol L^{-1} in the last days of the cruise. In contrast, surface isoprene concentrations did not change a lot during AL510 and were mostly varying between 20 and 60 pmol L^{-1}.

During each big station samples were taken from 6 different depths (3 samples within the MLD, 2 samples in the pycnocline, 1 sample below the pycnocline) in order to investigate the vertical distribution. Additionally near surface samples were taken from the rubber boat at each big station from 1 m, 50 cm and 10 cm depth as well as one sample from the SML.

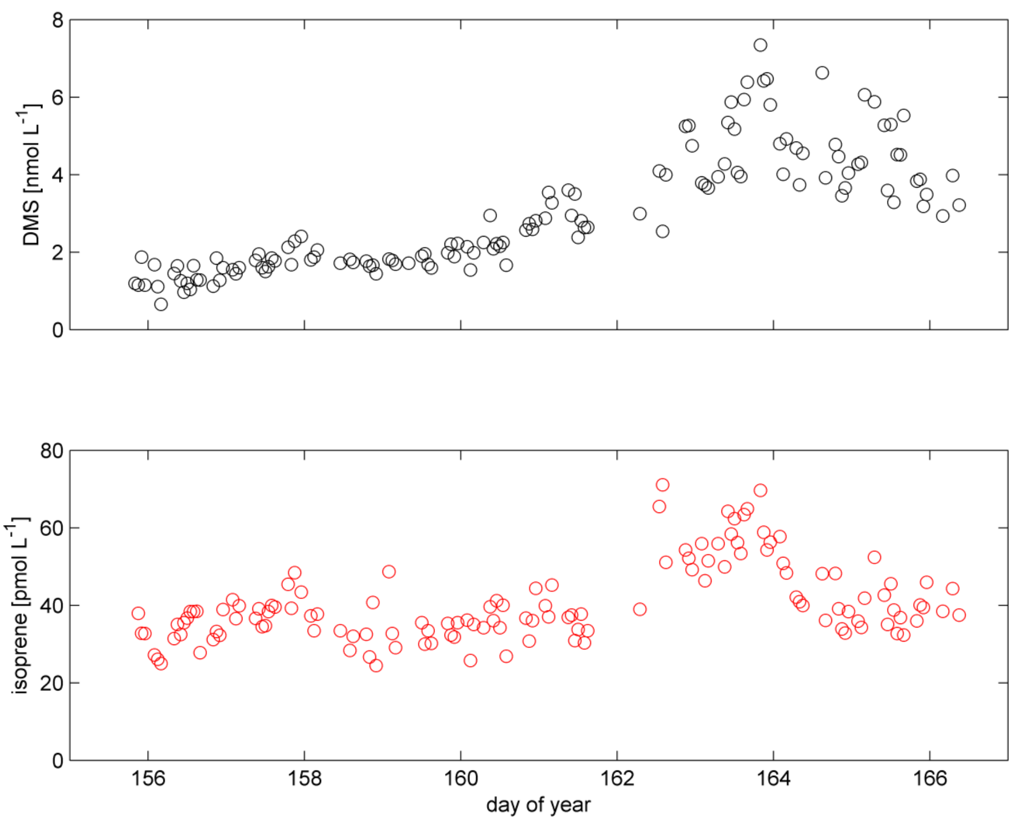

Figure 7: Hourly underway measurements of DMS and isoprene during AL510.

4.4 Biogenic characterization of the sea surface microlayer

During the Alkor expedition in June (AL510) the sea surface mircrolayer (SML) was monitored at 23 stations in total. Sample collection was conducted twice a day in the morning and the afternoon by applying the glass plate technique introduced by HARVEY and BURZELL (1972). Surface activity, as a proxy for substances exhibiting non-polar behavior and are, thus, enriched in the SML, was measured by the voltammetric approach after ĆOSOVIĆ and VOJVODIĆ (1998). Surface activity is quantified and expressed as equivalents of Triton X-100, an artificial surfactant. Surfactants were always enriched in the SML and in general exhibited constant concentrations throughout stations. However, the degree in which surfactant concentration deviated from the underlying water (ULW) differed considerably over stations (Figure 8).

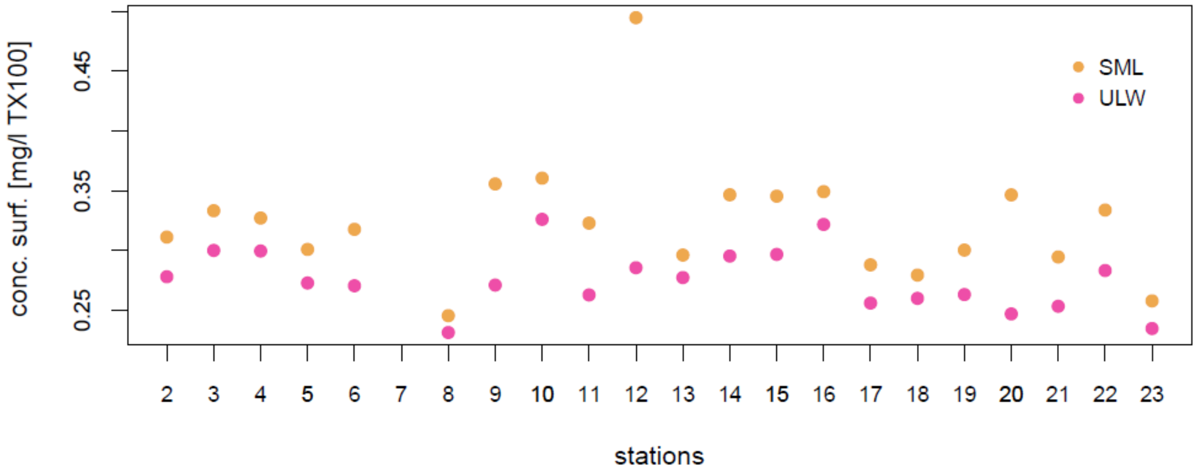

Figure 8: Surface active substances enrich in the sea surface microlayer (orange). Samples from the SML were taken by withdrawing a hydrophilic glass plate perpendicularly to the water surface and wiping off the attached surface water. Reference samples (pink) were taken from 20 cm depth with a bottle. Surfactants were constantly enriched in the SML.

For example, station 12 was extraordinarily enriched in surfactants compared to the next station 13 although time and location were close. Station 12 was sampled at very low winds. The sea surface was undisturbed by capillary waves assumingly dampened by high substance accumulation and could be identified as a slick. Outside this patch of high surfactant enrichment, capillary waves were visible. Further parameters, for example bacterio- and phytoneuston, were measured as well.

Phytoplankton cells exhibited low numbers during the first half of the cruise and increased considerably towards the end (Figure 9), which is also reflected in Chlorophyll a concentration (data not shown). Phytoneuston was depleted in the SML. This trend was especially clear during the second half of the cruise. One exception was station 12, exhibiting high enrichment of phytoplanktonic cells. As depicted in Figure 10, bacterial cell numbers often showed a similar distribution pattern between the SML and the ULW. Cell numbers were higher during the first week and declined in the middle of the cruise before increasing again towards the end.

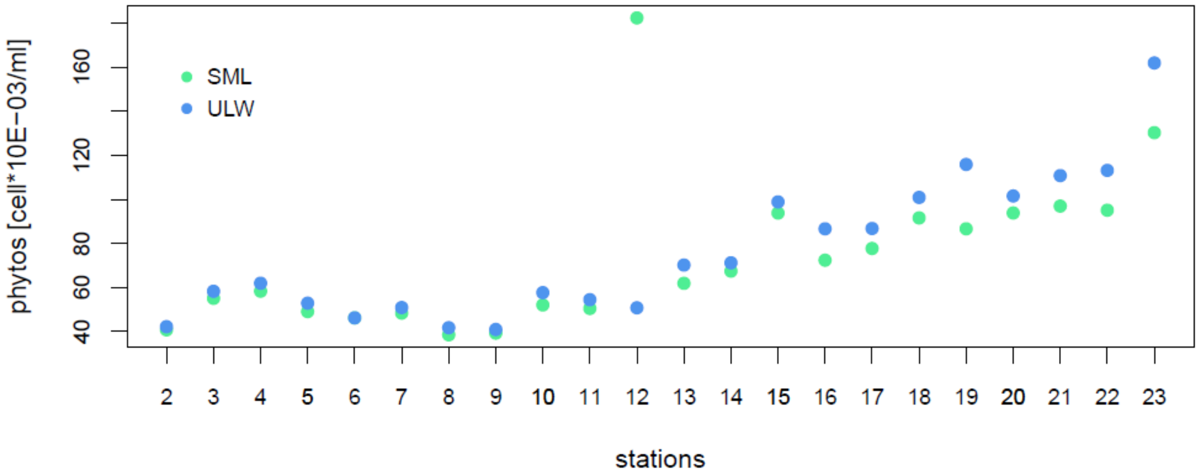

Figure 9: Phytoplankton cells increased in numbers towards the end of the cruise, while manifesting a depletion in the SML (green) compared to the ULW (blue). An exception of this pattern was station 12.

Surprisingly, surfactant concentration did not differ substantially during the cruise implying a rather uniform enrichment pattern not depending directly on bacterio- or phytoplankton abundances. When considering the assumed influence of surfactants on gas exchange processes, a uniform enrichment pattern would simplify the calculation of a factor describing the effect of surfactants on flux rates. However, the contribution of slick formation at low wind speed or at converging oceanic fronts should be taken into account as well. Additionally, analysis of carbohydrates and amino acid composition along with gel particles will help to unravel further traits of the SML and its supposed influence on gas exchange processes. This very regional data set over almost two weeks will provide an important contribution to the general description of the concept of the SML since data are normally gathered over large oceanic scales especially in regard to surface activity.

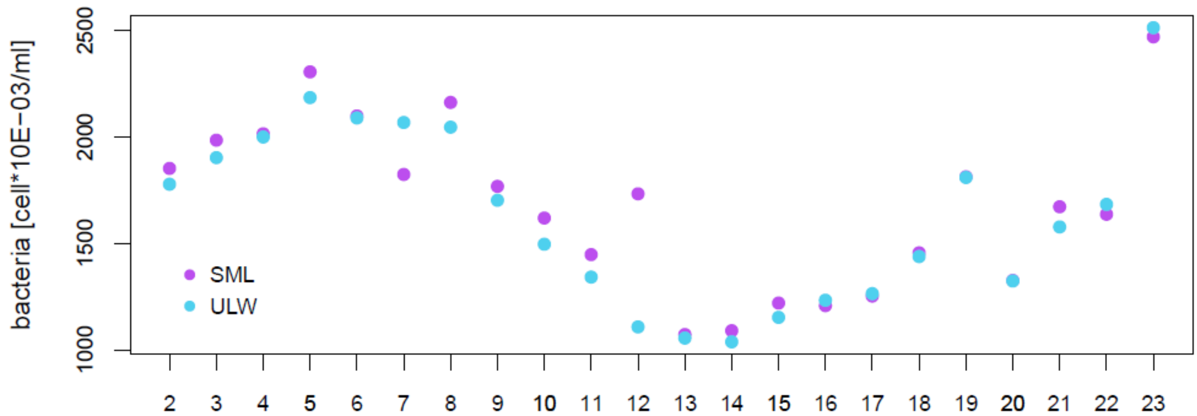

Figure 10: Bacterial cell numbers exhibited high abundances during the first station, but declined considerably towards the middle before a gain in numbers again towards the end. The enrichment pattern was in favor of the SML (purple), but was frequently equal to cell numbers detected in the ULW (blue).

4.5 Physical and chemical characterization of the sea surface microlayer

Lab-based analysis of the surfactant state of the sea surface microlayer (SML) has been performed by different analytical techniques including Vibrational Sum Frequency Generation Spectroscopy (VSFG, parameter: surfactant spectral intensity), tensiometry (parameter: surface tension), and Langmuir trough (LT) compression isotherms (parameter: surface pressure). These measurements complement the data on surfactant activity determined by phase sensitive AC voltammetry. During all rubber boat stations, SML samples have been collected both by the glass plate (triplicates) and the Garret screen (duplicates) sampling techniques (CUNLIFFE and WURL, 2014). Garret screen samples (duplicates) were also collected directly from the ship and bulk water samples were taken from the CTD casts at a depth of typically 18-25 m. Additional SML samples have been collected for later quantification of 3-hydroxy fatty acids using a LC/ESI/Orbitrap-MS setup at TROPOS (Manuela van Pinxteren, Leibniz Institute for Tropospheric Research, Leipzig, Germany). 3-hydroxy fatty acids have been suggested as biomarkers of endotoxins and Gram-negative bacterial community (LEE et al., 2004).

Vibrational Sum Frequency Generation

VSFG is a non-linear surface-sensitive laser spectroscopic technique used to probe vibrations of molecules located directly at the air-sea water interface (LAß and FRIEDRICHS, 2011). VSFG spectra have been recorded using a 532 nm up-conversion picosecond scanning type spectrometer (EKSPLA, Lithuania). In the context of SML analysis, VSFG can be used to detect organic surface active molecules (surfactants).

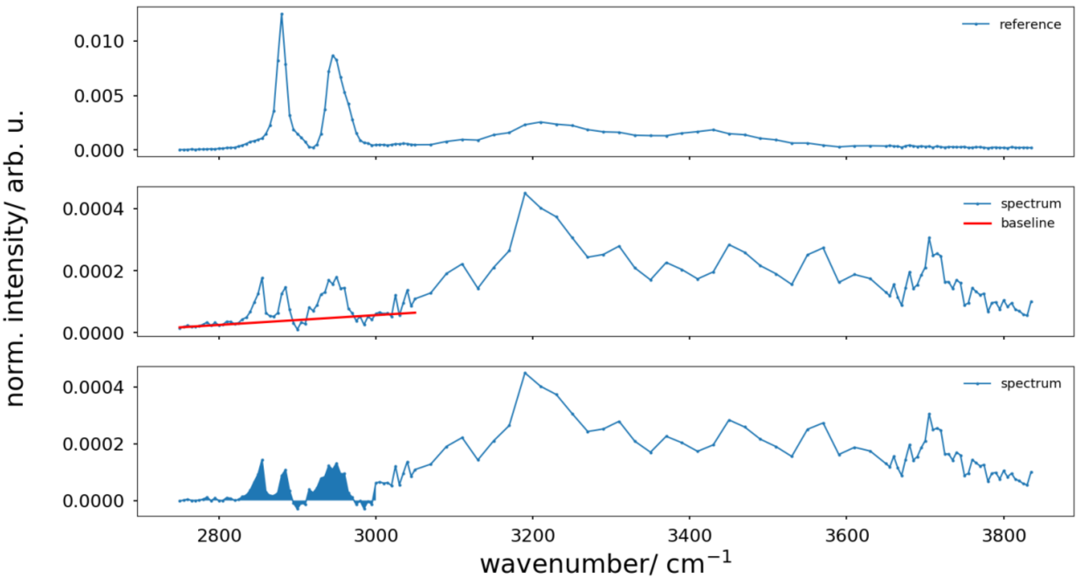

Figure 11: VSFG analysis of a typical SML sample: DPPC reference spectrum, baseline correction and integration of the CH region of the spectrum.

Figure 11 illustrates a typical sample analysis yielding a surface coverage of 13%. As the overall signal intensities turned out to be rather weak for the SML samples, a proper baseline subtraction was necessary, which has been implemented by an automatic Python analysis routine. The preliminary data analysis of all samples shown in Figure 12 reveals that during

AL510 the average surface coverage was low (< 10%) and close to the detection limit of the method. However, SML samples yield higher signals than bulk water samples, consistent with an enrichment of surfactants in the SML.

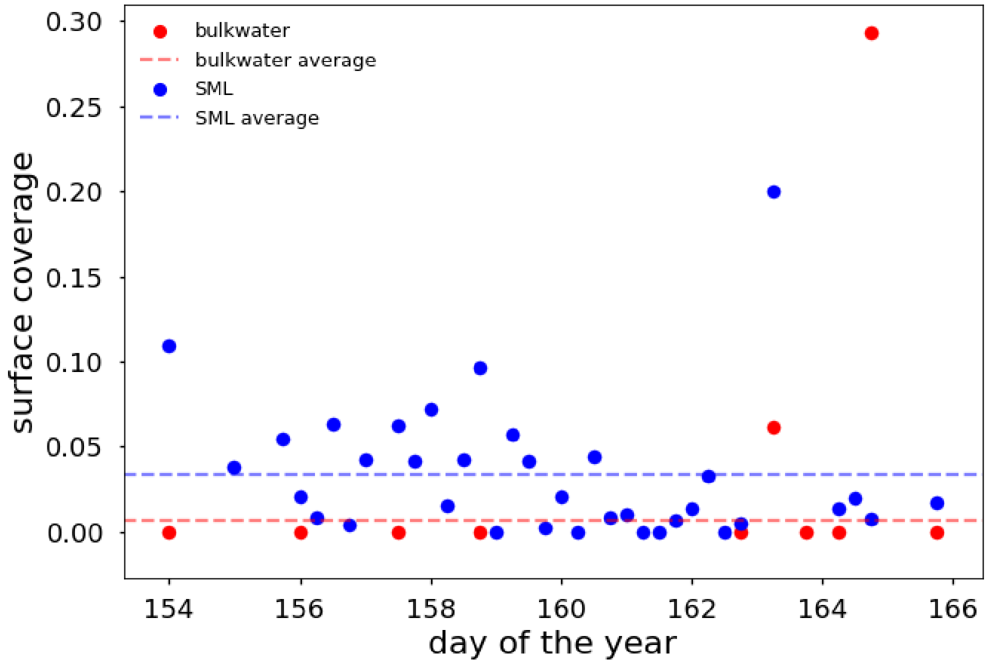

Figure 12: Surface coverage values detected from SFG analysis.

Tensiometry

Surfaces tension σ was measured by a Du-Noüy-type precision tensiometer (AquaPi Plus, Kibron, Finland) at room temperature (21 °C) with an accuracy of ±0.2 mN/m. The data in

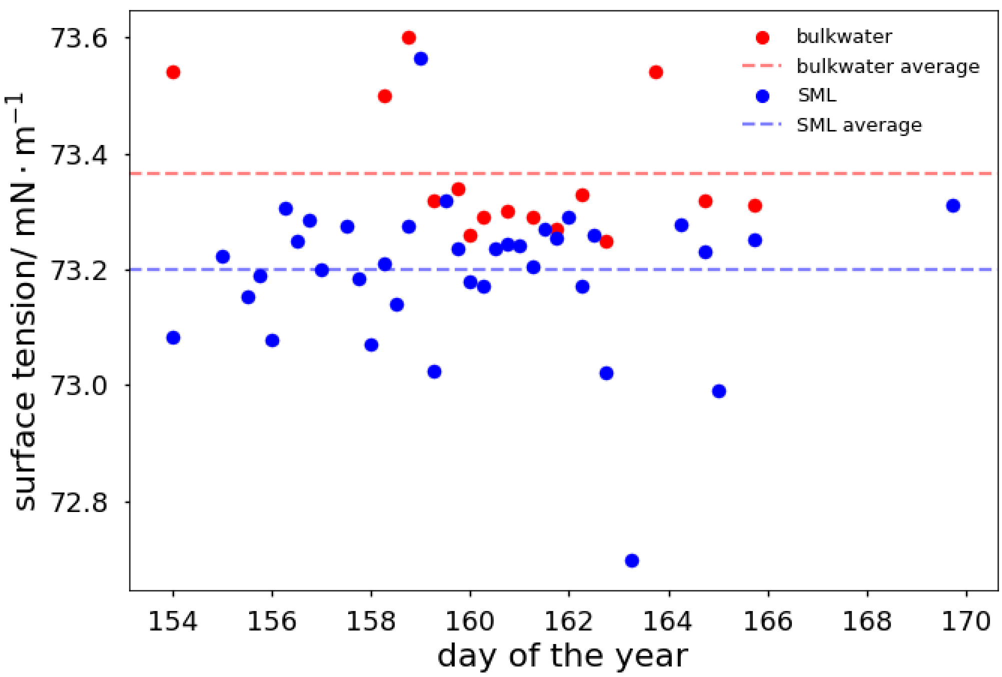

Figure 13: Average surface tension values (not yet corrected for salinity).

Figure 13 reveal values between 72.7 and 73.6 mN/m, which is close to the expected values of 73.2 ±0.3 mN/m for a clean water surface at salinity S = 19.5. The identified preliminary trend is: surface tensions are slightly lower for the SML samples compared to the bulk water. Note, however, that the observed trends are close to the accuracy of the measurements and still need to be corrected for salinity effects.

Langmuir Trough

Surface pressure isotherms were measured in a Langmuir trough (RK1, Riegler & Kirstein, Germany) by monitoring the surface pressure with a Wilhelmy balance as a function of the surface area with a precision of ±0.8 mN/m. The total compression ratio of the area A, $r=A_{start}/A_{end}$ which was achieved by moving Teflon barriers, was r=6.3. The surface pressure at maximum compression was taken as a measure for surfactant abundance. The data in Figure 14 indicate that the overall lower value for the bulk water sample (only one sample!) is consistent with surfactant enrichment in the SML.

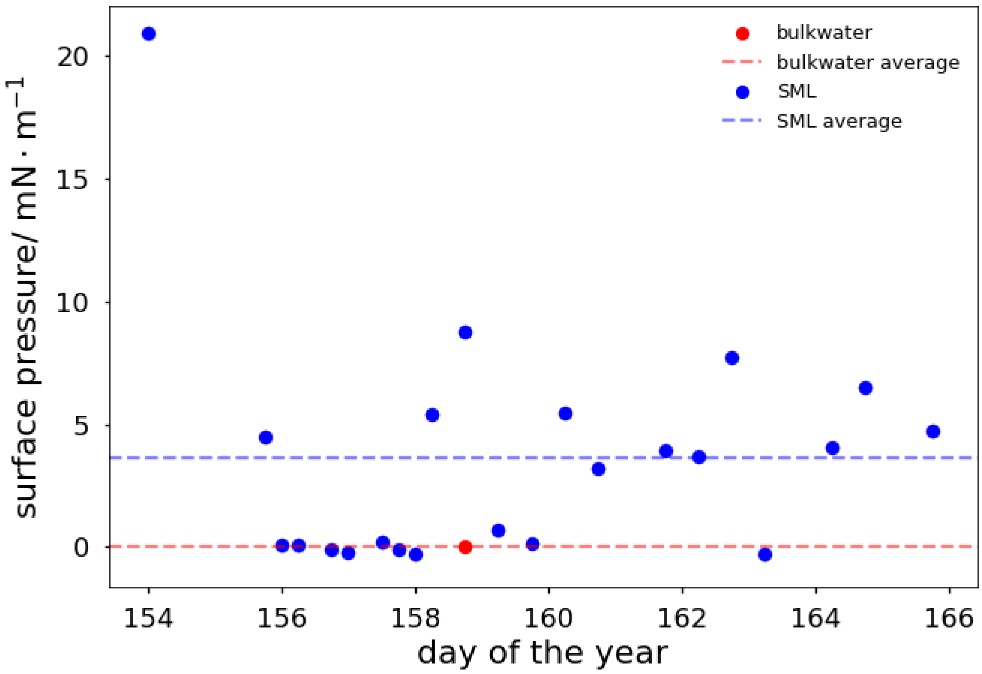

Figure 14: Average maximum surface pressure from Langmuir trough analysis.

5. Scientific equipment: instruments deployed into the water

- Drifter
- Microstructure sonde
- Moving CTD for tracer deployment
- CTD Seabird Electronics attached to a 12-bottle water sampler rosette
- Nortek Signature 1000 kHz transducer (using the ships ADCP)
- Deployment of rubber boat for glass plate and Garret screen sampling

6. Acknowledgements

Special thanks to the captain Jan Peter Lass and the whole crew of RV Alkor for their great support and advice during AL510. The cruise was partly funded by the US NSF. We thank GEOMAR Helmholtz Centre for Ocean Research Kiel for grant EP516 and additional funding by transatlantic Helmholtz Research School for Ocean System Science and Technology (HOSST).

7. Appendices

A station list (stationsplan_AL510.xls) was uploaded electronically together with this report.

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